Concentrated Solar Energy for Thermochemically Producing Liquid Fuels from CO_2 and H_2O

Peter G. Loutzenhiser, Anastasia Stamatiou, Willy Villasmil, Anton Meier, and Aldo Steinfeld

A two-step solar thermochemical cycle for producing syngas from H_2O and CO_2 via Zn/ZnO redox reactions is considered. The first, endothermic step is the thermolysis of ZnO to Zn and O_2 using concentrated solar radiation as the source of process heat. The second, non-solar, exothermic step is the reaction of Zn with mixtures of H_2O and CO_2 yielding high-quality syngas (mainly H_2 and CO) and ZnO; the latter is recycled to the first solar step, resulting in net reactions $CO_2 = CO+0.5O_2$ and $H_2O= H_2+0.5O_2$. Syngas is further processed to liquid fuels via Fischer-Tropsch or other catalytic reforming processes. State-of-the-art reactor technologies and experimental results are provided for both steps of the cycle.

INTRODUCTION

Intermittent sunlight can be efficiently stored in a chemical form by using concentrated solar energy as the high-temperature heat source to drive highly endothermic processes to produce solar fuels.[1,2] Our fuel target is synthesis gas (syngas, mainly CO and H_2), which can be processed via Fischer-Tropsch or other catalytic reforming processes to liquid hydrocarbons for the power and transportation sectors. Producing syngas with concentrated solar energy from H_2O and CO_2—the latter eventually captured from air[3]—represents a promising path towards sustainable energy utilization.

The solar thermolyses of H_2O[4] and CO_2[5] occur at ultra-high temperatures (>2,500 K), at which gaseous products must be separated to avoid recombination upon cooling or end up with an explosive mixture, making realization difficult. Conversely, the required process temperature can be reduced and the separation problem bypassed via two-step thermochemical cycles based on metal oxide redox reactions.[1,2,6–8] The Zn/ZnO redox pair emerges as one of the most promising for simultaneously splitting CO_2 and H_2O with favorable thermodynamics and the potential for high solar-to-fuel energy conversion efficiencies.[9–11] The cycle is schematically depicted in Figure 1. The first step is the thermolysis of ZnO using solar process heat, represented by Equation 1.

$$ZnO \rightarrow Zn+0.5O_2 \qquad \Delta H_{298.15\,K} = 350.5 \text{ kJ mol}^{-1} \qquad (1)$$

How would you…

…describe the overall significance of this paper?

It has been experimentally demonstrated that synthesis gas can be produced directly from CO_2 and H_2O using concentrated solar energy in a two-step thermochemical cycle based on Zn/ZnO redox reactions.

…describe this work to a materials science and engineering professional with no experience in your technical specialty?

Solar synthesis gas can be produced from CO_2 and H_2O in a two-step solar thermochemical cycle encompassing: (1) the endothermic thermolysis of ZnO to Zn and O_2 using concentrated solar irradiation for process heat; and (2) the non-solar, exothermic reaction of Zn with CO_2 and H_2O to produce CO/H_2 and ZnO. The ZnO is recycled back to the first step to complete the cycle.

…describe this work to a layperson?

A thermochemical cycle to produce mixtures of CO and H_2 from H_2O and captured CO_2 has been demonstrated using concentrated sunlight. Mixtures of CO and H_2 can be further processed to liquid fuels to provide clean energy for the transportation sectors.

The second step of the cycle is the non-solar, exothermic reaction of Zn with CO_2 and H_2O to generate simultaneously CO to H_2 (syngas) represented by Equation 2 in terms of the CO_2 molar fraction in CO_2+H_2O mixtures, β, varied between 0 and 1.

$$Zn+\beta CO_2 + (1-\beta)H_2O \rightarrow ZnO+ \beta CO + (1-\beta)H_2 \qquad -67.5 \text{ kJ mol}^{-1} < \Delta H_{298.15\,K} < -64.7 \text{ kJ mol}^{-1} \qquad (2)$$

The solid product of Equation 2 is ZnO, which is recycled back to the first step to close the materials cycle, resulting in a net reaction given by Equation 3. O_2 and syngas are produced in separate steps, thereby eliminating the need for gas separation. Since the steps are decoupled, the production of syngas can be carried out on demand at convenient sites and independent of solar energy availability.

$$\beta CO_2 + (1-\beta)H_2O \rightarrow \beta CO + (1-\beta)H_2 + 0.5O_2 \qquad 283.0 \text{ kJ mol}^{-1} < \Delta H_{208.15\,K} < 285.5 \text{ kJ mol}^{-1} \qquad (3)$$

The quality of the produced syngas, given by the molar ratios H_2:CO and CO_2:CO as well as by the presence of undesirable constituents, is crucial for further applications. Experimentation performed with laboratory-scale reactor prototypes for both cycle steps is presented to demonstrate the cycle viability.

REACTOR TECHNOLOGY AND EXPERIMENTATION

ZnO Thermolysis

The thermolysis of ZnO to Zn and O_2 has been successfully demonstrated in a 10 kW solar chemical reactor prototype shown schematically in Figure

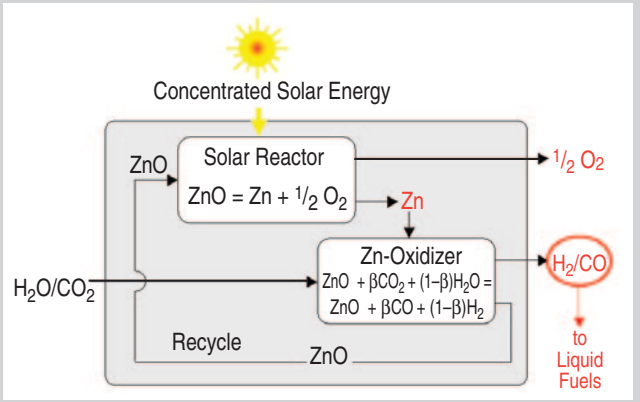

Figure 1. Schematic of the two-step cycle solar thermochemical cycle for producing syngas from CO_2 and H_2O via Zn/ZnO redox reactions.

2.[12] The main component is a rotating cylindrical cavity-receiver lined with sintered Al_2O_3 tiles mounted over ceramic matrix composite insulation, providing for the mechanical, chemical and thermal stability. The cavity-receiver contains a small opening—the aperture—to let in concentrated solar irradiation through a transparent quartz window. ZnO particles are introduced into the rotating cavity and forced against the cavity walls by centripetal acceleration, creating a packed-bed layer that is directly exposed to the high-flux irradiation. With this arrangement, the ZnO particles serve simultaneously the functions of radiative absorbers, thermal insulators, and chemical reactants. The reactor has a dynamic feeder that extends and retracts within the cavity, allowing for batches of an evenly distributed layer of ZnO particles of desired thickness over the entire cavity surface. An Ar flow injected through a set of radial and tangential nozzles creates an aerodynamic protection of the quartz window against condensable Zn(g). As the temperature increases, the ZnO particles dissociate to Zn(g) and O_2, which are carried to the reactor outlet. Experimentation was performed at Paul Scherrer Institute's high-flux solar simulator (HFSS):[13] an array of xenon arcs which provides an external source of intense thermal radiation that closely approximates the heat transfer characteristics of highly concentrating solar systems. Radiative fluxes incident at the aperture were measured optically with a calibrated charge coupled device camera on a Lambertian target. The O_2 concentration in the outlet flow was temporally monitored by a paramagnetic-based detector (Siemens Oxymat 6: sampling rate = 1 s^{-1}). The reactants used were ZnO particles (Alpha Aesar, –325 Mesh, 99%, mean particle diameter 0.22 mm). Type-B thermocouples were used to measure the temperature behind the Al_2O_3 tiles, $T_{backside}$. Figure 3 shows the mean solar concentration ratio, *C,* over the aperture (solid), mean $T_{backside}$ (dashed), and molar O_2 flowrates (dot-dashed) measured during a representative solar experimental run for a batch of 210 grams of ZnO particles. (The solar concentration ratio *C* is defined as the solar radiative flux normalized to 1 kW m^{-2}. *C* is often expressed in units of "suns".) As *C* was increased stepwise to around 2,745 suns by activating a series of Xe arcs, the reactor was slowly heated to minimize thermal stresses. $T_{backside}$ was maintained at just below 2,000 K by reducing *C* to 1,900 suns. The O_2 measured in the outlet gases, evidence of ZnO thermolysis, increased until reaching a maximum of $\dot{n}_{O_2} = 5\times10^{-4}$ mol s^{-1} after which *C* was incrementally reduced and O_2 was no longer detected at $t > 150$ min. Analysis of the solid particles collected downstream determined a Zn content of 54%, as a significant portion of Zn(g) underwent re-oxidation. To prevent Zn(g)/O_2 recombination, a quenching unit[14] was designed based on Ar injection at cooling rates from 20,000 to 120,000 K s^{-1}, yielding particles with a Zn content in the range 40–94% for Ar/Zn(g) dilutions of 170 to 1,500.

Zn Reaction with H_2O and CO_2

The reaction of Zn with H_2O and CO_2 has been studied in numerous reactor concepts.[15–18] Promising results to reduce CO_2[19] have been obtained in a packed-bed reactor containing micron-sized Zn particles supported on submicron-sized ZnO particles. The ZnO particles act as an inert substrate to prevent sintering and allow for easy recycling back to the first step. Experimentation was extended to simultaneously reduce H_2O and CO_2 with Zn in a 25 mm-i.d. quartz tube positioned vertically in a tubular furnace. Two type-K thermocouples were placed in the center of the tube at the inlet, T_{inlet}, and outlet, T_{outlet}, of the packed-bed. Zn particles (Sigma-Aldrich, 98+%, mean particle diameter 7.9 mm) and ZnO particles (Alpha Aesar, –325 Mesh, 99%, mean particle diameter 0.22 mm) were mixed

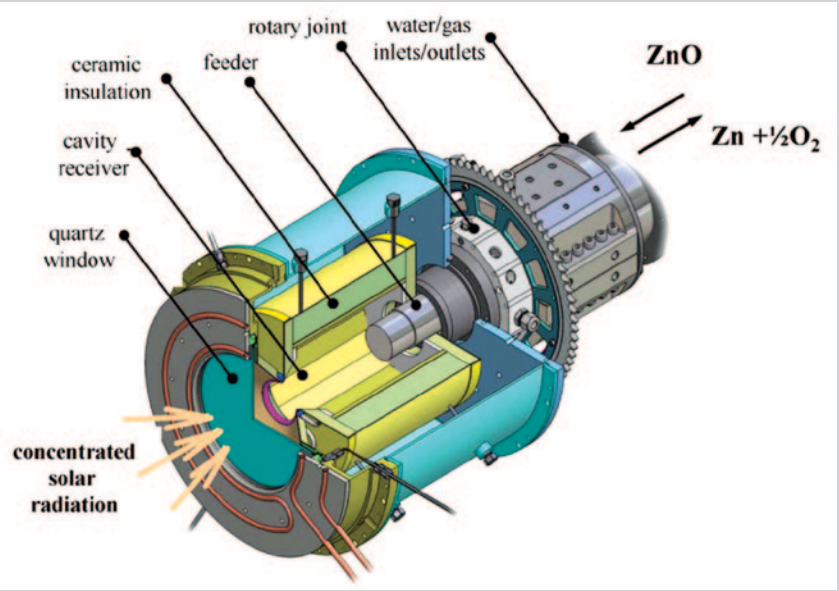

Figure 2. Schematic of the solar chemical reactor configuration.

to a total mass of 9 g and 30 Zn wt.%. The packed-bed was heated in Ar to T_{inlet} = 678 K as air was purged from the system. Once T_{inlet} and T_{outlet} stabilized, a reactive flow of 50%H_2O-CO_2 was introduced into the system (with no Ar dilution) and reacted with Zn to form H_2 and CO. The H_2O vapor was condensed from the outlet flow and outlet gas composition was determined by combined mass MS-GC. The results garnered from this representative experimental run are shown in Figure 4. As reactant flows were introduced into the system, CO and H_2 were immediately detected in equal molar amounts, with nearly complete temporal conversions of CO_2 and H_2O to syngas from $3 < t < 6$ min. In contrast to previous thermogravimetric analyses,[20] no competitive chemical kinetics between Zn with either H_2O or CO_2 were observed. The exothermicity of the reaction is seen by a small rise in T_{inlet}. Initially, the reaction occurred in the lower part of the packed-bed until Zn was fully converted to ZnO, delaying the rise in T_{outlet}. The heat was then conducted across the packed-bed and transported by the flow, resulting in an increase of T_{outlet} from just below 700 K to ~950 K. T_{outlet} then gradually decreased as the majority of the Zn was converted to ZnO.

The overall Zn-to-ZnO conversion based on the stoichiometry of Equation 3 was determined by the MS/GC measurements and integration of the molar flow rates over the duration of the experimental run. Zn-to-ZnO conversion was 82.1%.

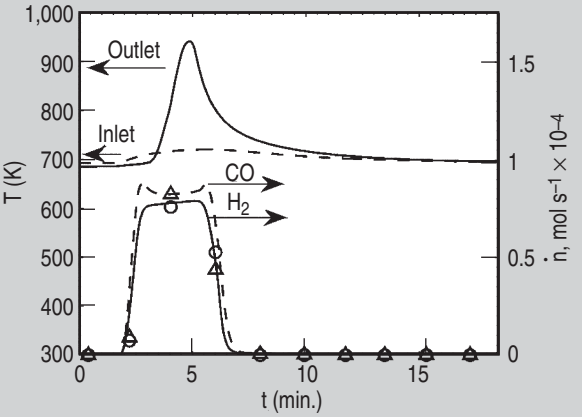

Figure 4. Temporal inlet (dashed) and outlet (solid) temperatures, and molar flow rates of CO (dashed, triangle) and H_2 (solid, circles) measured at the outlet of the Zn/ZnO packed-bed reactor for a representative experimental run with 3.004 g of Zn exposed to a 50%H_2O-CO_2 reacting flow.

CONCLUSIONS

Production of syngas from H_2O and CO_2 in a two-step solar thermochemical cycle via Zn/ZnO redox reactions was demonstrated with laboratory-scale reactor prototypes. The solar thermolysis of ZnO was demonstrated with a 10 kW solar reactor, while the reaction of Zn with CO_2-H_2O flows was realized in a packed-bed reactor designed to minimize sintering. The experimental results are currently used to validate heat/mass transfer reactor models,[21] which are applied for the optimization and scale-up of the technologies.

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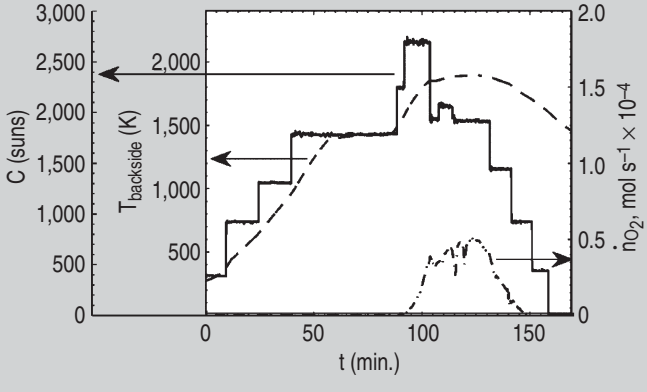

Figure 3. Measured solar concentration ratios (solid), reactor temperatures behind the Al_2O_3 tiles (dashed), and molar O_2 flow rates (dot-dashed) during a representative solar experiment run using the 10 kW solar reactor to thermolyze a batch of 210 g of ZnO particles to Zn(g) and O_2.

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